California Department of Food and Agriculture

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Environmental Analysis Section

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Pyrethroids in sediment

- Adapted from: A sonication extraction method for the analysis of pyrethroids, SIU, M.J. Lydy
- Sample may be frozen and batched
- Thaw sample-decant excess water
- Weigh out 20grams of sediment
- Add 5 grams Copper
- Add $MgSO_4$ mix until consistency of sand
- Add 75mL's 1:1 acetone:hexanes

Pyrethroids in sediment

- Shake sample at 185 rpm for 15 minutes
- Decant through $MgSO_4$ into boiling flask
- Repeat shaking with 75 additional mL's
- Decant through $MgSO_4$
- Rinse with 1:1 acetone:hexanes
- Rotovap to approx. 5mL's
- Ready for clean-up procedure

Pyrethroids in sediment water

- Weigh sample plus bottle
- Transfer water portion to separatory funnel
- Add 60mL's hexanes to sample bottle
- Shake for 30 seconds
- Transfer remaining sample to funnel
- Shake funnel for 2 minutes

Pyrethroids in sediment water

- Allow layers to separate
- Drain off lower water layer
- Transfer hexanes through Na_2SO_4 to dry
- Transfer water back into funnel
- Repeat extraction 2 more times
- Collect all hexanes in 500mL boiling flask

Pyrethroids in sediment water

- Rotovap to approx. 5mL's
- Ready for clean-up procedure

Clean-up procedures

- Condition a 2 gram florisil SPE cartridge
- Use 10mL's 15% ether in hexanes
- Follow with 20mL's hexanes
- Load entire extracted sample on SPE cartridge
- Rinse boiling flasks and load onto cartridge
- Elute pyrethroids using 30mL's 15% ether in hexanes

Clean-up procedures

- Evaporate sample to just dryness under gentle nitrogen stream
- Bring to final volume in hexanes
- GC/MS analysis final volume 1.0mL
- GC/ECD analysis final volume 2.0mL

LOD's and LOQ's in sediments

	LOD	LOQ
Bifenthrin	0.11ppb	1.0ppb
Fenopropathrin	0.11ppb	1.0ppb
Permethrins	0.14ppb	1.0ppb
Fenvalerates	0.11ppb	1.0ppb
λ-cyhalothrin	0.12ppb	1.0ppb
λ-cyhalothrin epimer	0.12ppb	1.0ppb

LOD's and LOQ's in sediments

	LOD	LOQ
Cypermethrins	0.11ppb	1.0ppb
Deltamethrin	0.10ppb	1.0ppb
Resmethrin	0.90ppb	1.5ppb

LOD's and LOQ's in water

	LOD	LOQ
Bifenthrin	1.8ppt	5.0ppt
Fenopropathrin	1.5ppt	15ppt
Permethrins	7.7ppt	15ppt
Fenvalerates	1.8ppt	15ppt
λ-cyhalothrin	1.2ppt	15ppt
λ-cyhalothrin epimer	1.1ppt	15ppt

LOD's and LOQ's in water

	LOD	LOQ
Cypermethrins	1.8ppt	15ppt
Deltamethrin	1.9ppt	15ppt
Resmethrin	3.8ppt	15ppt

Stability of pyrethroids in sediment water

- Adding 10mL's hexanes to 1.0 liter sediment water sample prolonged the sample storage stability

Stability of permethrins in sediment water (100 ppt spike) Recovery after 28 days

Compound	w/o hexane	w/hexane
Bifenthrin	54.8%	83.4%
Fenpropothrin	77.6%	95.5%
Permethrin-t	14.6%	93.8%
Permethrin-c	42.9%	91.2%
Fenvalerates	44.5%	81.5%

Stability of permethrins in sediment water (100 ppt spike) Recovery after 28 days

Compound	w/o hexane	w/hexane
λ-cyhalothrin	52.8%	86.8%
λ-cyhalothrin Epimer	54.2%	90.0%
Cyfluthrin	42.7%	86.6%
Cypermethrin	44.8%	82.3%

Positive attributes of the sediment method

- Simple sample preparation procedure
- Sample preparation uses low cost equipment and commercially available SPE cartridges
- Analysis is performed using GC configured with an ECD detector
- Confirmation is performed using GC configured with a mass selective detector (MSD)

Negative attributes of the sediment method

- Extraction may not be as complete as if done by accelerated solvent extraction (ASE)
- Cleanup procedure may not remove enough matrix contaminates for easy identification on GC/ECD
- May be necessary to raise the reporting limit on "dirty" sediment samples
- Detection limit for some compounds may be too high on the GC/MSD even in SIM mode

Pyrethroid methods

Questions?

CDFA would like to thank:

CALFED

USGS

For allowing us to be part of the pyrethroid method development